

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Protective Agents Against Textile Pests, Mould and Bacteria

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate, organised under the Laws of Germany, of 22c, Leverkusen-Bayerwerk, Germany, do hereby
5 declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention is concerned with agents for protecting textile materials, furs and skins against the attack of textile pests, mould and bacteria.

15 Specification No. 738,758 is concerned with the protection of textile materials, furs and skins against the attack of textile pests, mould and bacteria by impregnation with an agent containing as active ingredient a compound of the general formula $(\text{Hal}_x \text{R}_1 \text{SO}_2 \text{HN})_n \text{R}$,
20 wherein R is a mono- or divalent polynuclear carbocyclic radical, R_1 is an aliphatic hydrocarbon radical, x is an integer and n is 1 or 2, depending on the valency of R. In the polynuclear amines from which the amines are derived, the nuclei may be linked, according to the description of Specification No. 738,758, via intermediate members such as O, S, SO , SO_2 , CH_2 , $-\text{CH}=\text{CH}-$, CO or $\text{N}=\text{N}-$.

30 According to the present invention, textile materials, furs and skins are protected against the attack of textile pests, mould and bacteria by impregnating with an agent containing as active ingredient a haloalkyl-, haloaralkyl- and/or haloaryl-sulphonamide of an amino-
35 diphenylamine or N-imino-substituted aminodiphenylamine which is halogenated in one or both of the aromatic nuclei. In addition to a broad activity against keratin pests, such as moth larvae, fur and carpet beetles, and other
40 textile pests, such as termites, as well as against infection by bacteria and moulds, the new compounds are especially distinguished by killing completely larvae of moths within a

brief period of time. In these last properties, they particularly excel the compounds described in the above-mentioned specification.

The production of the aminodiphenylamine derivatives according to the invention is effected by methods known in principle by reacting the corresponding aminodiphenylamines, which may be further substituted by other groups such as alkyl, alkoxy, trifluoromethyl, trifluoromethylsulphonyl, chloromethylsulphonyl, alkylsulphonyl, alkylaminosulphonyl, aminosulphonyl, cyan, thiocyanate, nitro, halogen or haloalkylcarboxyl groups, with haloalkyl-, haloaralkyl- or haloaryl-sulphonic acid chlorides.

However, it is also possible subsequently to introduce halogen into the compounds according to the invention, for example by chlorination or bromination with free halogens or with sulphuryl chloride or sulphuryl bromide. Other known methods for introducing halogen, such as the reaction of diazonium salts to give fluorine or chlorine compounds or the exchange of movable groups for fluorine may also be employed.

The following examples are given for the purpose of illustrating the invention:—

EXAMPLE 1

PENTACHLORO - CHLOROMETHANE-SULPHONYL-2-AMINODIPHENYLAMINE

54 parts by weight 2-aminodiphenylamine are dissolved in 300 parts by weight anhydrous pyridine and 50 parts by weight chloromethane-sulphonic acid chloride are slowly added dropwise thereto with stirring and cooling with a mixture of ice and common salt. After stirring for several hours, the mixture is poured into water, the separated reaction product is dissolved in water with the addition of sodium hydroxide solution, stirred with carbon and Fuller's earth, filtered off with suction and the filtrate acidified. The precipitate formed is filtered by suction, washed with

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water until neutral and dissolved in ether. The ether extract filtered through carbon is distilled and the residue recrystallised from aqueous methanol. M.p. 116—117° C. Yield 31—40 parts by weight.

- 15 parts by weight of the chloromethanesulphonyl-2-amino-diphenylamine are dissolved in 300 parts *o*-dichlorobenzene, a little ferric chloride is added and chlorine introduced at a temperature rising to 40° C. until analysis of a worked-up sample shows a chlorine content corresponding to approximately 6 atoms of chlorine per molecule. The *o*-dichlorobenzene is then distilled off *in vacuo* and the residue worked up in a manner described above. 10—15 parts by weight of a slightly light-grey powder are thus obtained. M.p. 110—120° C.

EXAMPLE 2

- 20 Woolen or union fabrics are treated in organic solvents containing 0.1 per cent pentachloro-chloro - methanesulphonyl - 2-aminodiphenylamine described in Example 1. The material is thus protected against destruction by textile pests. Larvæ of moths are killed after a brief period of time.

Wool skins, fur material or feathers can be treated in a similar manner and are then protected in the same way.

EXAMPLE 3

- 30 Wool or union fabrics are treated at 60° C. in an aqueous solution of 0.1 per cent of the sodium salt (or another water-soluble salt) of pentachloro - chloromethane - sulphonyl - 2-amino-diphenylamine. After rinsing and drying, the material as such, even after repeated washing, is protected from destruction by textile pests and infection by bacteria and mould. Larvæ of moths applied to the material are completely killed after a brief period of time.

- In an analogous manner there may be prepared and employed the following amines: dichloromethanesulphonyl-, chloroethanesulphonyl-, trifluoro- or trichloromethanesulphonyl-, trichloroethanesulphonyl-, dichlorobenzylsulphonyl-, dichlorobenzenesulphonyl-, trichlorobenzenesulphonyl- or trifluoromethylchlorobenzenesulphonyl - amino-halo-diphenyl-amines.

- Instead of 2-aminodiphenylamine, there may also be used with good results for the production of effective compounds other aminodiphenylamines, such as 3 - aminodiphenyl-amine, 4-aminodiphenylamine, 2-amino - 4 - chlorodiphenylamine, 2 - amino-5-chloro-diphenylamine, 2 - amino-4¹-fluorodiphenylamine, 2 - amino-3-trifluoromethyl-4¹-chlorodiphenylamine, 2-amino - N - ethyldiphenylamine, 2-amino - N - chloroacetyldiphenylamine, 4 - amino - N - methanesulphonyldiphenylamine, 2-amino-4¹-methoxydiphenylamine or 4,4¹ - diaminodiphenylamine.

EXAMPLE 4

2 - amino - 4,4¹ - dichlorodiphenylamine is reacted in an analogous manner to that described in Example 1, with chloromethanesulphochloride. The chloromethanesulphonyl-2-amino-4,4¹-dichlorodiphenylamine crystallises from methanol in the form of colourless cubes, m.p. 180—181° C.

In a similar manner, chloromethanesulphonyl-2-amino - 4 - chloro - 4¹ - trifluoromethyl-diphenylamine (colourless needles from ethanol, m.p. 140° C.) is obtained from 2-amino-4-chloro - 4¹ - trifluoromethyl - diphenylamine (fibrous crystals, m.p. 112—113° C.). The compound, in a concentration of 0.5 per cent, shows a very good activity against moths.

By the action of chlorine on a solution in *o*-dichlorobenzene at 30—35° C. in the presence of ferric chloride, further chlorine atoms may be introduced, e.g. up to a total chlorine content of 37.0 per cent.

N-methyl - 2 - chloromethane - sulphonylaminodiphenyl-amine (m.p. 85—86° C.) may likewise be transformed by chlorination to give compounds having an excellent activity against moths.

From N-methyl - 4 - aminodiphenylamine (b.p. 210—215° C./15 mm Hg; m.p. 72—73° C.) there are obtained, according to the instructions given in Example 1, N-methyl-4-chloromethane - sulphonylamino - diphenylamine (m.p. 81—82° C.) and therefrom, for example, a chlorination product which is soluble in aqueous sodium hydroxide solution and may be again precipitated with acids (analysis: Cl=46.70%, S=5.0%).

From N - ethyl-4-amino - diphenylamine (b.p. 203—205° C./1 mm Hg; m.p. 49—50° C.) there is obtained chloromethanesulphonyl-4-amino-N-ethyldiphenylamine of m.p. 87—88° C. which may be further chlorinated to give a hexachlorodiphenylamine derivative (analysis: Cl 46.98%, N 4.8%, S 5.3%).

WHAT WE CLAIM IS:—

1. The protection of textile materials, furs and skins against the attack of textile pests, mould and bacteria, by impregnation with an agent containing as active ingredient a haloalkyl-, haloaralkyl- and/or haloaryl-sulphonamide of an aminodiphenyl-amine or N-imino - substituted aminodiphenylamine which is halogenated in one or both of the aromatic nuclei.

2. The protection of textile materials, furs and skins against the attack of textile pests, mould and bacteria according to Claim 1, wherein the haloalkyl-, haloaralkyl- and/or haloaryl-sulphonamide of an aminodiphenylamine or of an N-imino-substituted aminodiphenylamine halogenated in one or both of the aromatic nuclei is any of those hereinbefore specified.

3. The protection of textile materials, furs

and skins substantially as hereinbefore described.

4. The protection of textile materials, furs
and skins substantially as described in either
5 of Examples 2 and 3.

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